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Research Article

Phase evolution and properties of novel Al_2O_3-based poly-hollow microsphere (PHM) ceramics

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Abstract: In this paper, novel Al_2O_3-based poly-hollow microsphere (PHM) ceramics were prepared using Si_3N_4 and Al_2O_3 PHMs as pore-forming agents. The effect of Si_3N_4 and Al_2O_3 PHMs with different percentages on properties of Al_2O_3-based PHM ceramics was investigated. Through adjusting percentage of Al_2O_3 PHMs, Al_2O_3-based PHM ceramics with enhanced properties are achieved. X-ray diffraction (XRD) results show that main phases of Al_2O_3-based PHM ceramics vary from β-SiAlON (z value increases from 2.9 to 4) to Al_2O_3 with the increase of percentage of Al_2O_3 PHMs from 10% to 100%. The different phase compositions result in different properties of Al_2O_3-based PHM ceramics. With the increase of percentage of Al_2O_3 PHMs, porosity of Al_2O_3-based PHM ceramics gradually decreases, while their shrinkage, flexural strength, and fracture toughness firstly decrease and then increase. Using different kinds of ceramic PHMs as pore-forming agents, various novel and high-performance porous ceramics could be prepared via optimizing percentage of ceramic PHMs in the future.

Keywords: porous ceramics; poly-hollow microsphere (PHM); pore-forming agent; phase evolution; mechanical properties

1 Introduction

Recently, porous ceramics with high porosity, high specific surface area, low density, low thermal conductivity, and other unique properties have attracted much attention for their potential applications as catalyst supports, filters, thermal insulator, and bone substitutes, etc. [1–4]. At present, lots of processing routes have been used to prepare porous ceramics, such as direct foaming [5–8], freeze casting [9–12], replication of polymer sponge [13–15], and adding pore-forming agent [16–18], etc. Among all these methods, adding pore-forming agent has been extensively used to prepare porous ceramics due to its simple preparation process and low cost. However, irregular pores and non-uniform pore distribution could be observed in the prepared porous ceramics using common pore-forming agents (such as starch). Therefore, choosing proper pore-forming agent is considerably important. In recent years, ceramic poly-hollow microspheres (PHMs), a kind of special material with porous microstructures, have been

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successfully produced via combination of particle-stabilized foams and centrifugal atomizing technology [19,20], which could be used as novel promising pore-forming agent to prepare porous ceramics.

In 2014, Su *et al*. [19] prepared porous Al_2O_3 ceramics by gelcasting using Al_2O_3 PHMs as pore-forming agent. In addition, Qi *et al*. [20] proposed a novel route to prepare porous ceramics using Al_2O_3 PHMs. Via stacking Al_2O_3 PHMs in Al_2O_3 crucible with gentle tapping and knocking, the packed PHMs were directly sintered at 1400–1600 ℃ to prepare porous Al_2O_3 ceramics. Nevertheless, when lots of Al_2O_3 PHMs are used to prepare porous ceramics, they would contact with each other. Under this condition, it is found that the prepared porous Al_2O_3 ceramics usually fracture along Al_2O_3 PHMs and mechanical properties of the samples would be relatively low, which is attributed to low bonding strength among different Al_2O_3 PHMs. In order to improve the bonding strength among different Al_2O_3 PHMs, Yang *et al*. [21] coated Al_2O_3 PHMs with $CaSiO_3$ sintering additive via co-precipitation method, and then porous Al_2O_3 ceramics with good mechanical properties were successfully prepared by dry pressing using coated Al_2O_3 PHMs as pore-forming agent. Furthermore, porous Si_3N_4 ceramics were also successfully prepared using Si_3N_4 PHMs as pore-forming agent. Wu *et al*. [22] successfully prepared porous Si_3N_4 ceramics by gelcasting via adding 10–35 wt% Si_3N_4 PHMs (based on Si_3N_4 ceramic powders) as pore-forming agent. However, when large amount of Si_3N_4 PHMs (250 wt%, based on Si_3N_4 ceramic powders) are added into Si_3N_4 slurry to prepare porous Si_3N_4 ceramics with high porosity, the prepared porous Si_3N_4 ceramics mainly fracture along Si_3N_4 PHMs and their mechanical properties are relatively low, which is attributed to low bonding strength among different Si_3N_4 PHMs and that between Si_3N_4 PHMs and matrix [23]. Accordingly, porous Si_3N_4 ceramics with good mechanical properties using Si_3N_4 PHMs as pore-forming agent are difficult to fabricate.

Compared with Si_3N_4 PHMs, Al_2O_3 PHMs have completely different properties, such as different microstructure and lower sintering temperature, etc. In 2015, Zhang *et al*. [24] reported that using small amount of Si_3N_4 or Al_2O_3 PHMs as pore-forming agent (45 wt%, based on Si_3N_4 ceramic powders), the prepared porous Si_3N_4-based ceramics could achieve different pore morphologies and mechanical properties. Enlightened by the mentioned research, in our recent research, using Si_3N_4 and Al_2O_3 PHMs as pore-forming agents, these ceramic PHMs were added into Si_3N_4 slurry and porous Si_3N_4-based ceramics were finally prepared. However, although mechanical properties of porous Si_3N_4-based ceramics have been improved in some extent, the prepared porous Si_3N_4-based ceramics still fractured along ceramic PHMs. Accordingly, their mechanical properties should be further improved. Based on all the previous research, in this paper, Si_3N_4 and Al_2O_3 PHMs with different percentages were both added into Al_2O_3 slurry with low viscosity to prepare porous Al_2O_3-based ceramics. Here, this kind of novel porous Al_2O_3-based ceramics is defined as Al_2O_3-based PHM ceramics. The effects of Si_3N_4 and Al_2O_3 PHMs with different percentages on phase composition, microstructure, shrinkage, porosity, and mechanical properties of Al_2O_3-based PHM ceramics were investigated.

2 Experimental procedure

2. 1 Materials

Commercial Al_2O_3 ceramic powders (average particle diameter: 0.33 μm, specific surface area: 8.08 m^2/g, Almatis, Germany) were used to prepare low viscosity slurry in this study. Si_3N_4 and Al_2O_3 PHMs were commercially available materials (Hebei Yonglong Bangda New Materials Co., Ltd., China). According to our previous research, mechanical properties of the non-calcined ceramic PHMs (such as Si_3N_4 and Al_2O_3 PHMs) are so low that they would disperse in solvent (such as deionized water) and be destroyed in mixing process, thus ceramic PHMs should be firstly calcined at certain temperature to acquire enough mechanical properties. Under nitrogen atmosphere (0.1 MPa), Si_3N_4 PHMs were calcined at 1600 ℃ for 0.5 h. Meanwhile, Al_2O_3 PHMs were calcined at 1200 ℃ for 1 h in air. The average diameters of the calcined Si_3N_4 and Al_2O_3 PHMs were 69.79 and 95.86 μm, respectively. Meanwhile, the packing densities of the calcined Si_3N_4 and Al_2O_3 PHMs were 0.96 and 0.88 g/cm^3, respectively. Figure 1 shows the scanning electron microscopy (SEM) micrographs of the calcined Si_3N_4 and Al_2O_3 PHMs. It is found that many micro-pores exist in Si_3N_4 and Al_2O_3 PHMs, which would form final pores in the prepared ceramics.

In gelcasting process, deionized water was used as solvent. Acrylamide (AM, Sinopharm Chemical Reagent Co., Ltd., China), *N*,*N*′-

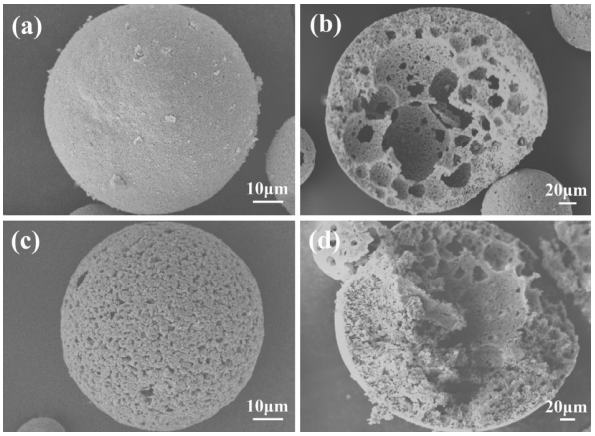

Fig. 1 SEM micrographs of (a) calcined Si_3N_4 PHMs and (b) their inner structures, and (c) calcined Al_2O_3 PHMs and (d) their inner structures.

methylenebisacrylamide (MBAM, Sinopharm Chemical Reagent Co., Ltd., China), and 30 wt% ammonium polyacrylate (PAA-NH_4, Zibo Jinghe Chemical Dyestuff Co., Ltd., China) aqueous solution were used as monomer, cross-linker, and dispersant, respectively. Meanwhile, initiator was 3 wt% ammonium persulfate (APS, Sinopharm Chemical Reagent Co., Ltd., China) aqueous solution and catalyst was N,N,N',N'-tetramethyl ethylenediamine (TEMED, Sinopharm Chemical Reagent Co., Ltd., China).

2. 2 Sample preparation

The flow chart of the preparation for Al_2O_3-based PHM ceramics by aqueous gelcasting using Si_3N_4 and Al_2O_3 PHMs as pore-forming agents is the same as that shown in Ref. [22]. Concentration of the premix solution was 13 wt%, and ratio of AM and MBAM was 20:1. Al_2O_3 ceramic powders and dispersant (1 wt% PAA-NH_4, based on Al_2O_3 ceramic powders) were added into premix solution to make slurry with solid loading of 20 vol%. Strong aqua ammonia was used to adjust pH value of slurry at about 10. After ball milling for 12 h, the slurry was degassed for 10 min, and then the maximum calcined ceramic PHMs (158 wt%, based on Al_2O_3 ceramic powders) were added into slurry. In this process, the percentages of Si_3N_4 and Al_2O_3 PHMs were different. Table 1 shows the samples with different percentages of Si_3N_4 and Al_2O_3 PHMs. When adding ceramic PHMs into slurry, continual stirring is necessary, which could ensure Si_3N_4 and Al_2O_3 PHMs distributing uniformly in slurry. Meanwhile, during mixing process, slurry should be stirred slightly to avoid introducing many air bubbles. Afterwards, degassing process was performed again. Catalyst (TEMED, 0.16 mL per 1 g AM) and initiator (APS, 0.16 mL per 1 g AM) were added into slurry, then molds with slurry were heated at 70 ℃ for 5 min to accelerate gelation process. Binder was burned out from the dried green samples at 600 ℃ for 1 h in air. Under nitrogen atmosphere (0.1 MPa), all the samples were sintered at 1750 ℃ for 1 h.

Table 1 Samples with different percentages of Si_3N_4 and Al_2O_3 PHM content

Sample	Percentage of Si_3N_4 PHM content (%)	Percentage of Al_2O_3 PHM content (%)
A	90	10
B	70	30
C	50	50
D	30	70
E	10	90
F	0	100

2. 3 Characterization

Phase analysis was conducted by X-ray diffraction (XRD) method using Cu Kα radiation (D8 ADVANCE, Bruker, Karlsruhe, Germany). Microstructures of the samples were observed by environment scanning electron microscope (ESEM, SSX-550, Shimadzu, Kyoto, Japan). Shrinkage of Al_2O_3-based PHM ceramics was calculated with the following formula:

$$S = \frac{D_0 - D}{D_0} \times 100\% \quad (1)$$

where D_0 and D represent diameters of the green sample before drying and sintered ceramics, respectively. Porosity of Al_2O_3-based PHM ceramics was measured by Archimedes' method. Flexural strength and fracture toughness of Al_2O_3-based PHM ceramics were measured using the mechanical testing machine (AG-2000A, Shimadzu, Kyoto, Japan). Flexural strength of the specimens with dimension of 3 mm × 4 mm × 40 mm was measured via three-point bending test, and the loading rate was 0.5 mm/min. Fracture toughness of the specimens with dimension of 2.5 mm × 5 mm × 30 mm and notch length of 2.5 mm was measured via single edge notched beam (SENB) method, and the loading rate was 0.05 mm/min.

3 Results and discussion

3. 1 Phase compositions and microstructures of the samples

Figure 2 shows the SEM micrographs of Al_2O_3-based

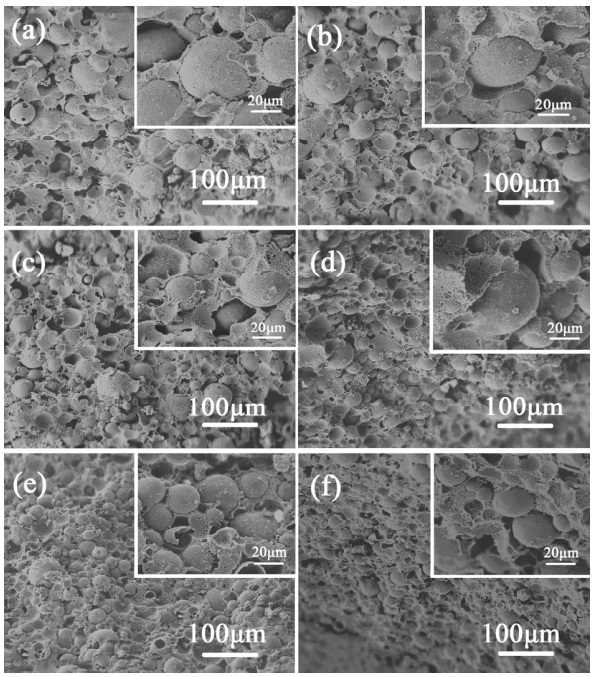

Fig. 2 SEM micrographs of Al_2O_3-based PHM green samples: (a) sample A, (b) sample B, (c) sample C, (d) sample D, (e) sample E, (f) sample F.

PHM green samples. Regarding all the prepared green samples, although percentage of Al_2O_3 PHMs is different, it is found that microstructures of Al_2O_3-based PHM green samples are similar. Meanwhile, ceramic PHMs are intact and distribute uniformly in the samples, and gaps among different ceramic PHMs are filled with Al_2O_3 matrix.

Figure 3 shows the XRD patterns of Al_2O_3-based PHM ceramics. Main phases of the samples gradually vary from β-SiAlON (z value increases from 2.9 to 4) to Al_2O_3. When percentage of Al_2O_3 PHMs increases from

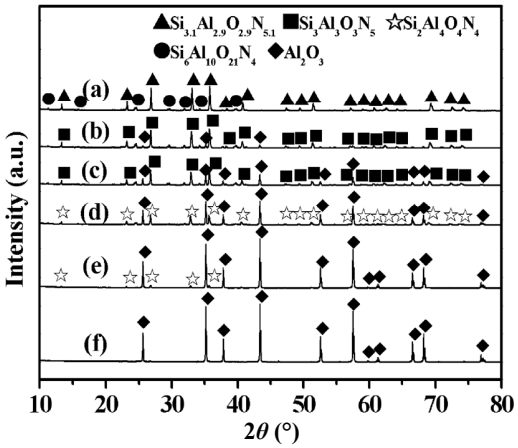

Fig. 3 XRD patterns of Al_2O_3-based PHM ceramics: (a) sample A, (b) sample B, (c) sample C, (d) sample D, (e) sample E, (f) sample F.

10% to 30%, main phase of Al_2O_3-based PHM ceramics is β-SiAlON (see Figs. 3(a) and 3(b)). In addition, when percentage of Al_2O_3 PHMs is 50%, it is found that β-SiAlON and Al_2O_3 co-exist in Al_2O_3-based PHM ceramics (see Fig. 3(c)). When percentage of Al_2O_3 PHMs is low, the extensively distributed Al_2O_3 matrix and the added Al_2O_3 PHMs could fully diffuse into Si_3N_4 to form $Si_{3.1}Al_{2.9}O_{2.9}N_{5.1}$ (β-SiAlON, $z=2.9$). With the increase of percentage of Al_2O_3 PHMs, more Al_2O_3 diffuses into Si_3N_4, thus z value of the formed β-SiAlON gradually increases, and $Si_3Al_3O_3N_5$ (β-SiAlON, $z=3$) and $Si_2Al_4O_4N_4$ (β-SiAlON, $z=4$) gradually appear in the samples. When percentage of Al_2O_3 PHMs increases from 70% to 100%, main phase of Al_2O_3-based PHM ceramics is Al_2O_3 (see Figs. 3(d), 3(e), and 3(f)). Moreover, when percentage of Al_2O_3 PHMs varies from 10% to 70%, small amount of $Si_6Al_{10}O_{21}N_4$ (X-SiAlON) exists in the samples. Table 2 shows the lattice parameters of formed β-SiAlON ($z=$ 2.9, 3, 4). With the increase of z value, the lattice parameters of the formed β-SiAlON increase. The ion substitution of Si^{4+} and N^{3-} by Al^{3+} and O^{2-} would cause the increase of the lattice parameters. With the increase of percentage of Al_2O_3 PHMs, more ion substitutions occur in the samples. Therefore, the lattice parameters of β-SiAlON increase with the increase of percentage of Al_2O_3 PHMs. The different phase compositions of the samples would greatly affect their performance, which would be discussed in the following section.

Figure 4 shows the SEM micrographs of Al_2O_3-based PHM ceramics. Regardless of percentage of Al_2O_3 PHMs, microstructures of the prepared Al_2O_3-based PHM ceramics are similar. Meanwhile, lots of pores exist in the samples. Meanwhile, intact ceramic PHMs could not be observed and all the samples fracture across ceramic PHMs, which demonstrates bonding strength between ceramic PHMs and matrix is high enough. Because matrix in these samples is Al_2O_3 and Al_2O_3 PHMs are added into Al_2O_3 matrix, the sintering process would be greatly improved by Al_2O_3 sintering additive, and bonding strength between ceramic PHMs and matrix is so high that the samples fracture mainly

Table 2 Lattice parameters of formed β-SiAlON ($z=$ 2.9, 3, 4)

z value	Lattice parameter (nm)	
	a	c
2.9	0.7664	0.2963
3	0.7681	0.2975
4	0.7692	0.2990

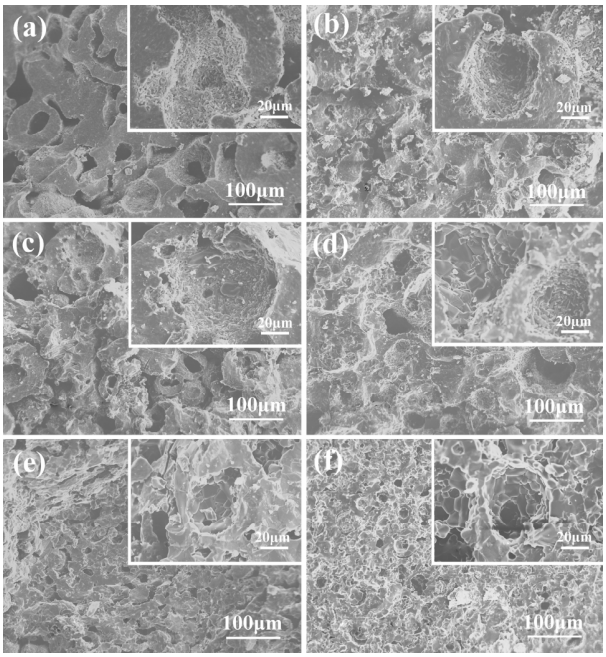

Fig. 4 SEM micrographs of Al_2O_3-based PHM ceramics: (a) sample A, (b) sample B, (c) sample C, (d) sample D, (e) sample E, (f) sample F.

across ceramic PHMs. Furthermore, with the increase of percentage of Al_2O_3 PHMs, amount of rod-like β-SiAlON grains in the samples gradually decreases and large amount of equiaxed Al_2O_3 grains gradually appear in the samples.

3. 2 Properties of the samples

Figure 5 shows shrinkage of Al_2O_3-based PHM ceramics. With the increase of percentage of Al_2O_3 PHMs, shrinkage of Al_2O_3-based PHM ceramics decreases firstly and then increases. When percentage of Al_2O_3 PHMs is 50%, shrinkage of the samples reaches the minimum value (27.00%). When percentage of Al_2O_3 PHMs increases to 100%, shrinkage of the samples increases rapidly up to 38.58%. According to the previous research [25], when more and more Al_2O_3 diffuses into Si_3N_4, lattice parameters of the formed β-SiAlON gradually increase, thus their microstructures become more and more incompact. According to Fig. 3, it is found that main phase of samples A and B is β-SiAlON, while that of samples D, E, and F is Al_2O_3. However, for sample C, there are two main phases, namely β-SiAlON and Al_2O_3. When the percentage of Al_2O_3 PHMs increases, the lattice parameters of β-SiAlON gradually increase, thus cell volume of β-SiAlON increases. When percentage of Al_2O_3 PHMs increases up to 50%, the increase of cell

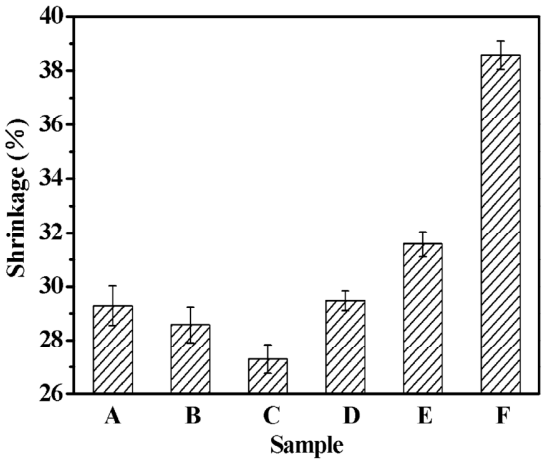

Fig. 5 Shrinkage of Al_2O_3-based PHM ceramics.

volume of β-SiAlON would compensate the sintering shrinkage of the sample to a great extent, thus the shrinkage of sample C is the lowest. Meanwhile, due to the existence of compensation effect between sintering shrinkage of sample and the increase of cell volume of β-SiAlON, the shrinkage of samples A, B, and C decreases slowly. Nevertheless, for samples D, E, and F, the main phase is Al_2O_3, which takes a main role in affecting the shrinkage of sample. In this case, with the increase of percentage of Al_2O_3 PHMs, the shrinkage of the samples increases rapidly.

Figure 6 shows porosity of Al_2O_3-based PHM ceramics. With the increase of percentage of Al_2O_3 PHMs, porosity of Al_2O_3-based PHM ceramics decreases gradually. The sintering temperature of Al_2O_3 PHMs is relatively low, and they act as both pore-forming agent and sintering additive. With the increase of percentage of Al_2O_3 PHMs, less and less pores exist in the samples, thus porosity of the samples gradually decreases.

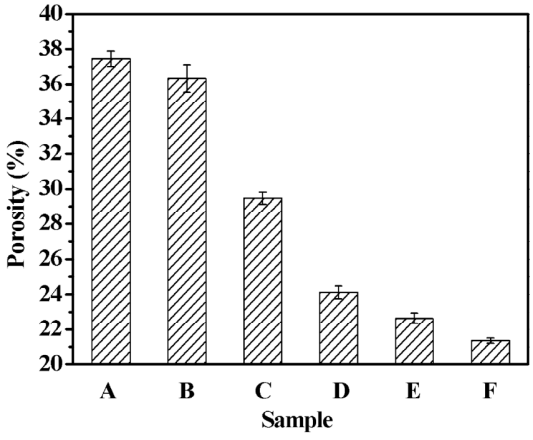

Fig. 6 Porosity of Al_2O_3-based PHM ceramics.

Figure 7 shows mechanical properties of Al_2O_3-based PHM ceramics. With the increase of percentage of Al_2O_3 PHMs, flexural strength and fracture toughness of Al_2O_3-based PHM ceramics both decrease firstly and then increase, and the variation trend is similar with that shown in Fig. 5. According to the XRD results, with the increase of percentage of Al_2O_3 PHMs, z value of β-SiAlON ($Si_{6-z}Al_zO_zN_{8-z}$, $0 \leqslant z \leqslant 4.2$) gradually increases. When z value is high, lattice parameters of β-SiAlON increase, while strength of the atomic covalent bonding in their crystal structures decreases, thus their microstructures become incompact [25]. Accordingly, with the increase of z value, hardness, flexural strength, and other properties of the samples could be deteriorated [26]. Therefore, mechanical properties of the prepared Al_2O_3-based PHM ceramics gradually decrease. When percentage of Al_2O_3 PHMs increases up to 50%, main phases of the samples are β-SiAlON ($Si_3Al_3O_3N_5$, $z = 3$) and Al_2O_3. The formed β-SiAlON grains have relatively incompact microstructures, thus their mechanical properties are relatively low. Furthermore, the shrinkage of sample is the lowest in this case, so the bonding strength between β-SiAlON and Al_2O_3 (the main phases) is also the lowest. Accordingly, the prepared samples have the lowest mechanical properties. With the continual increase of percentage of Al_2O_3 PHMs, main phase of the samples is Al_2O_3, properties of samples take on those of Al_2O_3 ceramics, thus mechanical properties of Al_2O_3-based PHM ceramics gradually increase. When percentage of Al_2O_3 PHMs is 100%, flexural strength and fracture toughness of the samples reach up to 155.23 MPa and 2.84 MPa·m$^{1/2}$, respectively.

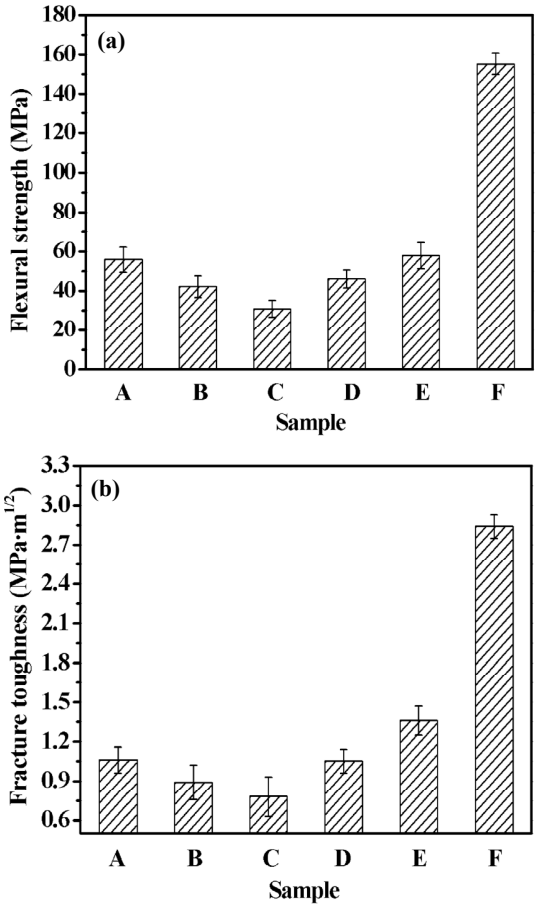

Fig. 7 (a) Flexural strength and (b) fracture toughness of Al_2O_3-based PHM ceramics.

4 Conclusions

In this paper, novel Al_2O_3-based PHM ceramics were successfully prepared by aqueous gelcasting using Si_3N_4 and Al_2O_3 PHMs as pore-forming agents. Through adjusting percentage of Al_2O_3 PHMs, bonding strength between ceramic PHMs and matrix is greatly improved and Al_2O_3-based PHM ceramics with good properties are prepared. When percentage of Al_2O_3 PHMs increases from 10% to 100%, main phases of the samples gradually vary from β-SiAlON (z value increases from 2.9 to 4) to Al_2O_3. It is found that phase compositions could highly affect properties of Al_2O_3-based PHM ceramics. When percentage of Al_2O_3 PHMs increases from 10% to 30%, main phase of the samples is β-SiAlON (z value increases from 2.9 to 3), and porosity, shrinkage, flexural strength, and fracture toughness of the samples gradually decrease. When percentage of Al_2O_3 PHMs is 50%, main phases of the samples are β-SiAlON ($z = 3$) and Al_2O_3, porosity of the samples decreases, while their shrinkage, flexural strength, and fracture toughness reach the minimum values. When percentage of Al_2O_3 PHMs increases from 70% to 100%, main phase of the samples is Al_2O_3, porosity of the samples decreases, while their shrinkage, flexural strength, and fracture toughness gradually increase. It is a novel method to prepare porous ceramics with controllable performance using different kinds of ceramic PHMs as pore-forming agent in the future.

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References

[1] Xue W, Huang Y, Xie Z, *et al*. Al_2O_3 ceramics with well-oriented and hexagonally ordered pores: The formation of microstructures and the control of properties. *J Eur Ceram Soc* 2012, **32**: 3151–3159.

[2] Yan W, Lin X, Chen J, *et al*. Effect of TiO_2 addition on microstructure and strength of porous spinel ($MgAl_2O_4$) ceramics prepared from magnesite and $Al(OH)_3$. *J Alloys Compd* 2015, **618**: 287–291.

[3] Cui X, Tang S, Zhou H. Mesoporous alumina materials synthesized in different gel templates. *Mater Lett* 2013, **98**: 116–119.

[4] Dash SR, Sarkar R, Bhattacharyya S. Gel casting of hydroxyapatite with naphthalene as pore former. *Ceram Int* 2015, **41**: 3775–3790.

[5] Yin L, Zhou X, Yu J, *et al*. New consolidation process inspired from making steamed bread to prepare Si_3N_4 foams by protein foaming method. *J Eur Ceram Soc* 2013, **33**: 1387–1392.

[6] Yu J, Yang J, Li S, *et al*. Preparation of Si_3N_4 foam ceramics with nest-like cell structure by particle-stabilized foams. *J Am Ceram Soc* 2012, **95**: 1229–1233.

[7] Sciamanna V, Nait-Ali B, Gonon M. Mechanical properties and thermal conductivity of porous alumina ceramics obtained from particle stabilized foams. *Ceram Int* 2015, **41**: 2599–2606.

[8] Soh E, Kolos E, Ruys AJ. Foamed high porosity alumina for use as bone tissue scaffold. *Ceram Int* 2015, **41**: 1031–1047.

[9] Tang Y, Miao Q, Qiu S, *et al*. Novel freeze-casting fabrication of aligned lamellar porous alumina with a centrosymmetric structure. *J Eur Ceram Soc* 2014, **34**: 4077–4082.

[10] Li W, Lu K, Walz JY. Effects of solids loading on sintering and properties of freeze-cast kaolinite–silica porous composites. *J Am Ceram Soc* 2013, **96**: 1763–1771.

[11] Xia Y, Zeng YP, Jiang D. Microstructure and mechanical properties of porous Si_3N_4 ceramics prepared by freeze-casting. *Mater Design* 2012, **33**: 98–103.

[12] Zuo KH, Zeng Y-P, Jiang D. Properties of microstructure-controllable porous yttria-stabilized ziroconia ceramics fabricated by freeze casting. *Int J Appl Ceram Tec* 2008, **5**: 198–203.

[13] Chen F, Yang Y, Shen Q, *et al*. Macro/micro structure dependence of mechanical strength of low temperature sintered silicon carbide ceramic foams. *Ceram Int* 2012, **38**: 5223–5229.

[14] Silva SA, Brunelli DD, Melo FCL, *et al*. Preparation of a reticulated ceramic using vegetal sponge as templating. *Ceram Int* 2009, **35**: 1575–1579.

[15] Delbrücke T, Gouvêa RA, Moreira ML, *et al*. Sintering of porous alumina obtained by biotemplate fibers for low thermal conductivity applications. *J Eur Ceram Soc* 2013, **33**: 1087–1092.

[16] Xu G, Ma Y, Cui H, *et al*. Preparation of porous millite–corundum ceramics with controlled pore size using bioactive yeast as pore-forming agent. *Mater Lett* 2014, **116**: 349–352.

[17] Nishijima H, Suzuki Y. Microstructural control of porous Al_2TiO_5 by using various starches as pore-forming agents. *J Ceram Soc Jpn* 2014, **122**: 565–569.

[18] Chen F, Shen Q, Yan F, *et al*. Pressureless sintering of α-Si_3N_4 porous ceramics using a H_3PO_4 pore-forming agent. *J Am Ceram Soc* 2007, **90**: 2379–2383.

[19] Su Z, Xi X, Hu Y, *et al*. A new Al_2O_3 porous ceramic prepared by addition of hollow spheres. *J Porous Mater* 2014, **21**: 601–609.

[20] Qi F, Xu X, Xu J, *et al*. A novel way to prepare hollow sphere ceramics. *J Am Ceram Soc* 2014, **97**: 3341–3347.

[21] Yang J-L, Xu X-X, Wu J-M, *et al*. Preparation of Al_2O_3 poly-hollow microsphere (PHM) ceramics using Al_2O_3 PHMs coated with sintering additive via co-precipitation method. *J Eur Ceram Soc* 2015, **35**: 2593–2598.

[22] Wu J-M, Zhang X-Y, Yang J-L. Novel porous Si_3N_4 ceramics prepared by aqueous gelcasting using Si_3N_4 poly-hollow microspheres as pore-forming agent. *J Eur Ceram Soc* 2014, **34**: 1089–1096.

[23] Wu J-M, Zhang X-Y, Wang Y-L, *et al*. Effect of sintering temperature on properties of porous Si_3N_4 ceramics with Si_3N_4 poly-hollow microspheres as pore-forming agent. *J Chin Ceram Soc* (*Eng.*) 2014, **1**: 129–134.

[24] Zhang X-Y, Wu J-M, Yang J-L. Pore morphology designs of porous Si_3N_4-based ceramics using Si_3N_4 and Al_2O_3 poly-hollow microspheres as pore-forming agents. *Mater Lett* 2015, **144**: 39–42.

[25] Xie ZP. *Structural Ceramics*. Beijing: Tsinghua University Press, 2011: 452.

[26] Tanaka I, Nasu S, Adachi H, *et al*. Electronic structure behind the mechanical properties of β-SiAlONs. *Acta Metall Mater* 1992, **40**: 1995–2001.